Porosity and Solvent-induced Pore Reconstruction in Coal as Determined by Neutron and Light Scattering Techniques

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Most naturally occurring coals are high surface area, microporous materials. Depending upon the rank of the coal, void volumes which range from as little as a few percent to as much as 50% are measured. Since the void dimensions extend to molecular size range, the corresponding surface areas are large (ranging to several hundred meters per cubic centimeter of solid). There are many consequences of the small void dimensions and large surface areas[1]. The importance of porosity in determining internal mass transport characteristics of coals is widely accepted. Similarly, mass transport, and hence porosity, is assumed to be an important determinant of reactivity.

The explicit connection between mass transport through the void volume and reactivity has never been convincingly demonstrated. Recently, Suuberg has demonstrated that mass transport control can be used to alter the products in a coal pyrolysis reaction[2]. Even this leaves unanswered many fundamental questions involving porosity and reactivity.

In this paper, we review some of the work carried out in this laboratory which was designed to "fingerprint" and semi-quantitatively characterize coal porosity and examine the effect of a variety of simple physical and solvent treatments on the coal. Commonly employed methods for porosity determination generally examine coal under specialized conditions and use specific solvents or gases[3]. Such measurements do not directly permit one to answer the question of fundamental importance -- what is the void structure during the reaction or while a solvent is in contact with the coal.

We have employed a variety of non-intrusive optical techniques to examine the pore structure of coal both dry and in the presence of solvents. We discuss results from two--small-angle neutron scattering and visible light scattering. To date our experiments have been performed at ambient temperature. However, there is no fundamental limitation to extending these techniques to elevated temperature regimes. Indeed, since many common metals are nearly "transparent" to neutrons and visible light can be coupled into closed systems with fiber-optic techniques, the usual problems associated with in-situ measurements of coal

under technologically interesting conditions can be overcome.

Small-angle Neutron Scattering

Small angle scattering techniques have been applied to a large variety of structural studies of liquid and solid phase materials(4). The two radiation sources which have proven to be of importance for solid-state studies are x-rays and neutrons. We chose neutrons for two principal reasons: 1). The contrast, and hence the scattering efficiency, of included mineral matter with respect to organic components is small (by comparison to x-rays). Therefore, scattering due to mineral matter inclusions will not overwhelm the scattering due to the presence of voids. 2). The pore-to-carbon (or mineral) matrix contrast can be controlled by the addition of organic liquids containing hydrogen and deuterium atoms. Thus, the "visibility" of the voids can be controlled thereby allowing the scattering from the voids to be isolated from other sources of scattering (e.g. matrix structure, mineral inclusions). The wavelength of neutrons employed are generally in the 4 to 8 Angstrom range. This allows void structures in the range of about 2 to 40 nm to be examined and corresponds well with the micro pore and transitional pore regimes probed by nitrogen-BET and CO_2 adsorption-desorption measurements(3).

Light Scattering

Scattering studies employing visible light have several advantages as compared to those utilizing neutrons. The equipment needed is more readily available. Additionally, the size range probed is larger (ca. 50 nm to 2 micrometers) and is probably more important in determining the overall internal mass transport than is the micro and transitional pore volume. However, studies employing visible light have been impeded by the high optical density of coal. We have employed sub-micron thickness wafers of coal to overcome the latter and permit the direct measurement of the scattering and absorption strengths of coal which is immersed in a series of common organic solvents(7,8). The wavelength dependence of the absorption gives, in principal, information about the molecular components. The wavelength dependence of the scattering provides information about the sizes and shapes of the voids.

We have employed two different methods to perform these measurements. In early work, a microspectrophotometer operating in the near-UV to near-IR region of the spectrum was employed(8). This apparatus could not separate absorptivity changes from scattering changes. Hence data interpretation assumed that the absorptivity was unchanged upon solvent treatment. This assumption was confirmed in later work(9) in which a spectrometer was employed that was

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capable of separately determining the scattering and absorptivity.

Void Volume Exhibits Adsorption Selectivity

We have carried out studies in which dried coal was exposed to water vapor(5,9), the vapor of various organic liquids(6,9), and slurried with water and several common organic liquids(7,9). In the case of exposure to aqueous media (either vapor or liquid), penetration into the void volume followed by condensation was found to be difficult. This was first noted in early neutron scattering experiments(5) in which D_2O vapor was found to incompletely fill the smallest voids of a broad void distribution. Subsequently we observed penetrability difficulties with some of the non-aqueous solvents used in the light(9) and later neutron scattering(7) experiments. One experimental consequence of the difficulty of aqueous penetration into dry coal is that extra care had to be taken to insure complete (aqueous) liquid penetration into the powdered coal slurries used both in later neutron scattering(7) as well as light scattering(9) work.

Reversible Deformation of Coal Thin-sections

In the case of sample preparation for light scattering, fascinating physical effects could be observed when the coal thin-sections were first placed under vacuum and then exposed to a moderate pressure (50 Torr < P < 760 Torr) of "non-wetting" liquids or vapors. Unlike particulate coal, a coal thin-section is easily deformed by "wrapping-up" on itself. Immersion in some vapors and liquids (esp. water) resulted in a non-penetrating "skin" on the thin-section surface. When the system pressure was increased (either by allowing access to air or controllably introducing a sub-atmospheric pressure of helium), the thin-section "collapsed". If this process was carried out in a controlled manner, the thin-section could be "rolled-up" in a spiral fashion upon application of system pressure and "unrolled" to its original shape and dimensions by removal of the higher system pressure. Our interpretation of this phenomena is that the non-wetting vapor or liquid skin prevents the system pressure from being equalized in the interior of the thin-section. The thin-section must then deform to relieve the resulting stress. The easiest physical transformation which will achieve the stress reduction is one which minimizes the "surface" area. In view of the geometry of the thin-section (0.5 micron thick by 1 mm by 1 mm) and the fact that cutting-induced fractures are present in the "plane" of the thin-section, the "rolling-up" of the thin-section is a reasonable method to relieve the induced stress. What is surprising is that the structural integrity in the "plane" of the thin-section is so great that the thin-section can be reversibly compressed into a microscopic area and returned

to its original shape. We were able to repeat such reversible cycles at least 4 to 6 times before any noticeable physical damage to the thin-sections were evident. Even then, the resulting damage appeared to be confined to tearing along previously weakened boundaries. These observations, though qualitative and empirical, are the most graphic demonstration that this author has even seen in support of coal being an internally crosslinked, gel-like material.

Void-size Distribution is Continuous

The void-size distribution was examined in dry coal as well as coal treated with liquids which are generally believed to have little or no effect on the internal pore structure (5,7,9). In our earliest neutron scattering work, power-law-like behavior was observed from coals both dry and exposed to the equilibrium vapor pressure of H_2O and D_2O (5). Such power-law behavior can arise from void or matrix structures having different geometrical properties, including fractal. Similar behavior has been reported by Bale and Schmidt and interpretted as arising from an internal surface fractal structure (10). In view of the limited range length scale range over which data is collected, the applicability of the fractal model as opposed to an unspecified broad and continuous distribution is questionable.

In subsequent neutron scattering work we confirmed the presence of near power-law behavior and continuous void-size distributions(7). The extension of scattering curves to probe larger length scales was achieved by observing the visible light scattering(9). Though the interaction of the radiation with the coal is different, the principal light scattering mechanism is that of pore-to-void contrast. Therefore, the light and neutron scattering curves can be "joined" in order to observe the scattering function over a wider length scale. From such a curve analysis, it is clear that the existence of a broad, continuous distribution of void-sizes is confirmed. Clear power-law behavior indicating fractal behavior is not observed. Comparisons with computer generated scattering curves for reasonable fractal structures indicates that exact adherence to a fractal model is unlikely(11). However, the near power-law behavior is evidence that a model incorporating an overall fractal structure with allowance for local deviations may be appropriate.

Micro Pores Are Unchanged by Non-swelling Solvents and Exhibit Penetrability Restrictions

Neutron scattering measurements of coal slurried in cyclohexane indicates that the micro and transitional pore distribution is unchanged from that in dried coal. Some

difficulty in filling of the smallest pores was observed. Differential scattering measurements can be used to obtain information about the unfilled voids. They were found to be modeled well by long, needle-like voids having a cross-sectional diameter of about 2 nm. Contrast matching techniques employing a series of cyclohexane/perdeutero-cyclohexane and H_2O/D_2O slurries indicate that the overall void surface is largely comprised of aliphatic and aliphatic carboxylic acid species. Therefore, the penetrability restrictions observed might indicate that intermolecular hydrogen-bonding interactions and a polar surface prevent complete penetration of the non-polar cyclohexane. This hypothesis contrasts with the usual restricted pore-entrance model. The polar-surface, hydrogen-bonding model implies that a large number of carboxylic acid dimers and multimers will be present on the surface of the void. Some confirmatory evidence that such species exist in large proportion is available from in-situ FT-i.r. experiments performed in this laboratory(12).

Transitional and Macro Pores Are Easily Deformed

The structural "rigidity" upon solvent saturation which is observed in the small void-size regime is not observed in the larger size regime probed by light scattering. Though broad continuous distributions were observed in coal immersed in each of 7 liquids, significant changes in the details of the distribution after liquid immersion were observed with all liquids(9). Surprisingly, even those liquids which result in little or no swelling (e.g. water, cyclohexane) show clear evidence for void-structure alterations. The void-structure alterations were accompanied, in all cases, by an increase of the total void-volume contributing to the light scattering. Though the size-range probed by light is broad, it does not encompass all sizes. Therefore, the mechanism for the volume increase is currently uncertain. One possibility is the "swelling" of voids which are smaller than the resolution limit of the light scattering measurement. Concomitant changes in the low-angle portion of the neutron scattering curves are ambiguous in this regard.

Light-transmission Losses Through Coal Result From Light Scattering

The origin of the high optical density of coal has long been the subject of study and debate(12). Our early work indicated that the overall light-transmission through coal can be substantially increased by immersion in liquid(8). This was subsequently confirmed in studies in which we simultaneously measured both the absorptivity and the light scattering through coal immersed in 7 different liquids(9). The liquids were chosen to cover a range of interaction

properties from non-swelling to highly-swelling and optical properties from low to high index of refraction.

In the mid-visible region of the spectrum, light scattering losses were found to account for over one half of the total light attenuation through coal. Additionally, negligible changes in the absorptivity were found upon immersion in the wide variety of solvents. The latter is not surprising since the molecular components leading to the absorptivity are unchanged. Significant contributions to the absorptivity due to aromatic-aromatic stacking interactions is unlikely in view of the observed insensitivity of the absorptivity to immersion in the variety of liquids chosen.

The large component due to light scattering and its significant wavelength dependence has important consequences on the interpretation of transmission and reflectivity data. Measurements made on coal undergoing any type of physical or chemical change will be accompanied by changes in pore geometry and possibly pore filling. Therefore, over most of the visible region of the spectrum, the dominant cause of light transmission changes will result from structural changes to the coal rather than chemical composition changes. Such transmission changes are frequently assumed to arise from absorptivity, hence molecular structure changes, and are interpreted in terms of chemical alteration to the coal. This cannot be correct. One example is the interpretation of color changes which occur when thin-sections having a thickness of several microns are treated with solvent or subject to reaction. By virtue of the strong wavelength dependence of the scattering, small changes in thickness or pore geometry will substantially alter the transmission losses, in this case. A color change can easily arise by altering the spectrum of the light transmitted through a coal thin-section or reflected from its surface.

While such light scattering effects have not been systematically dealt with in optical studies of coal, their quantification offers the possibility of preparing semi-transparent coal slurries in which the true changes to molecular absorption can be observed. In any such studies, it is critical that the wavelength dependence of the transmission and reflection spectrum be examined in order that the optical changes be properly assigned. A particularly interesting possibility is the measurement of internal network structure changes using polarized absorption and scattering measurements.

Summary

Neutron small-angle scattering and light scattering measurements of low and medium rank (sub-bituminous and bituminous) coals indicate that the void structure of coal

is best modeled as a continuous distribution of voids rather than a well defined discrete pore distribution. Solvent permeation studies indicate that the smallest voids are difficult to fill with a liquid when the liquid does not easily wet the surface. Solvent penetration into the void structure reduces the overall optical density of the coal with respect to the transmission of visible light. Analysis of the transmitted and diffusely scattered light indicates that the solvent partially index matches the void to the coal matrix with the resulting transmission increase. Analysis of the wavelength dependence shows that all imbibed liquids alter the internal pore and matrix geometries and generally results in an overall increase in the volume fraction of pores observed.

These observations imply that the pore structure is not a uniquely defined volume even at ambient temperature. Rather it is quite fluid and easily deformed upon application of mechanical stress. The light and neutron scattering from coal can be used to provide a fingerprint of the pore (and complimentary matrix) structure. Changes in the scattering can provide considerable detail about induced changes to the structure. Combined light scattering and absorption measurements, such as described herein, can be used to separate, uniquely, the chemical changes from the physical changes which occur during coal treatment and reactions.

Acknowledgement

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